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Title: SOLUBLE HYDROXYLATED VINYL COPOLYMERS FOR VARNISHES AND LACQUERS, AND METHODS OF PREPARING THEM

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The invention's objective is hydroxylated vinyl copolymers which can be used in the manufacture of varnishes and lacquers; it also concerns a process whereby the said copolymers can be manufactured.

French Patent No. 77 04891 discloses a process for preparing soluble copolymers which incorporate hydroxyl groups and which can be hardened with organic polyisocyanates.

The invention's main objective is to arrive at new copolymers which have the same uses as those described in the above-mentioned patent, but obtained by a new process. In accordance with the invention, instead of proceeding with a reaction between acrylic acid and glycidic esters of α-alkylalkanemonocarboxylic acids and/or of α,α-dialkylalkanemonocarboxylic acid, one carries out a reaction between glycidyl acrylate and/or glycidyl methacrylate and saturated fatty acids.

The products of the invention are obtained by copolymerization in a suitable solvent of specific monomers, which are present in the desired proportions, at an elevated temperature and in the presence of a conventional polymerization initiator of the type with free radicals. As a variant or as a supplement, use may be made of chain-transfer agents which make it possible to obtain resins with low molecular weight.

In general, the copolymers of the invention have the following composition:

(a) 0 to 50% by weight of styrene,

(b) 0 to 72% by weight of methyl methacrylate, with the proviso that the sum of these two components reaches at least 23%,

(c) 10 to 30% by weight of hydroxyalkyl acrylate and/or methacrylate,

(d) 0 to 2% by weight of methacrylic acid, (0 to 20% in claims)

(e) 8 to 20% by weight of glycidyl methacrylate and/or glycidyl acrylate, esterified by:

(f) 10 to 25% by weight of fatty acids which are saturated in C 8 to C12, straight chain or branched, of natural or synthetic origin.

The parts (a) to (f) together total 100%.

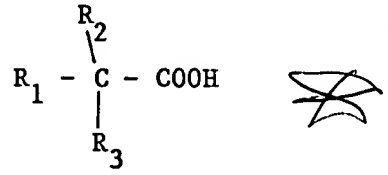
In accordance with the invention, it is not absolutely necessary to add methacrylic acid. This addition is simply desirable since it tends to improve the adhesion. It is possible, moreover, to replace this small amount of methacrylic acid by acrylic acid, the carboxylic groups acting as an internal catalyst during the cross-linking by the isocyanates.

In accordance with the process of the invention, in order to produce the copolymerization, the polymerization solvent is introduced into a reactor and heated to the chosen copolymerization temperature, which will lie between 70 and 170°C as a function of the nature of the initiator and of the polymerization solvent. While stirring, there is slowly added the above mixture of the compounds (a) to (f) along with the polymerization initiator. It is preferable to carry out this operation over a period of several hours. Next, the polymerization temperature is maintained for several hours. If judged useful, more polymerization initiator may be added.

The copolymerization is carried out in solution in solvents which do not react with the isocyanates as, for example, alkyl benzenes such as toluene, xylenes, esters such as ethyl acetate, butyl acetate, the ester ethers of diols such as methyl glycol acetate, ethyl glycol acetate.

As hydroxy alkyl acrylates or methacrylates, use may be made of 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate.

As saturated fatty acids, use may be made of linear or branched acids which are of natural or synthetic origin. As examples of linear fatty acids, mention may be made of pelargonic acid and lauric acid. As examples of branched fatty acids, mention may be made of versatic acid 10 produced by the SHELL company, the cekanoic acids C8, C9 and C10 by the UGINE-KUHLMANN company. Versatic acid 10 is a synthetic acid constituted by a mixture of saturated tertiary carboxylic acids having a total of 10 atoms of carbon, and which can be represented by the formula



where R_1 and R_3 are alkyl radicals whose sum incorporates 8 atoms of carbon.

The Cekanoic acids C_8, C_9 and C_{10} are respectively: dimethylhexanoic acid (general formula $C_8H_{17}COOH$), trimethyl 3,5,5-hexanoic acid (general formula $C_9H_{19}COOH$), dimethyloctanoic acid (general formula ($C_{10}H_{21}COOH$).

The esterification of the epoxidized monomer by the fatty acid may be effected before, during or after the polymerization. In the last two cases, the addition of the methacrylic acid or acrylic acid evoked above is not possible.

In order that the process for preparing the substances of the invention is better understood, a description will now be given of two examples of preparation of two copolymers.

EXAMPLE 1

292 g of ethyl glycol acetate are introduced into a 4 liter round-bottomed flask fitted with a stirrer, a thermometer, and a water-separator surmounted by an ascending coolant. The charge is heated to refluxing (at about 155°C), whereupon there is added, over a period of 3 hours while maintaining the refluxing, a mixture composed of:

methyl methacrylate	231 g
styrene	478.5 g
hydroxyethyl acrylate	158 g
hydroxyethyl methacrylate	160 g
glycidyl methacrylate	197 g
tertiododecyl mercaptan	34.4 g
AZDN (azobisisobutyronitrile)	22.8 g
xylene	487 g.

At the end of this addition, there are added 239 g of Cekanoic acid C10, after which there is added the mixture:

AZDN	4.55 g
xylene	195 g.

The addition is effected over a period of 1 hour while continuing to reflux (at about 145°C). Following this addition, refluxing is continued for another 4 hours prior to cooling.

EXAMPLE 2

A mixture consisting of 292 g of ethyl glycol acetate and 487 g of xylene is heated to refluxing (at about 145°C) after which the following mixture is added in a regular manner over a period of 3 hours while maintaining the refluxing:

methyl methacrylate	231 g
styrene	486 g
hydroxyethyl acrylate	158 g
hydroxyethyl methacrylate	138 g
methacrylic acid	15 g
glycidyl/cekanoic C10 acid methacrylate adduct	436 g
tertiododecyl mercaptan	34.4 g
AZDN	22.8 g

After this addition, refluxing is continued for an extra 30 minutes after which there is added the mixture

AZDN	4.55 g
xylene	195 g,

the addition being made over a period of 1 hour while continuing to reflux (at about 145°C). After this addition, refluxing is continued for 1 hour prior to cooling.

The glycidyl methacrylate/Cekanoic C10 acid adduct mentioned above was prepared as follows:

The following mixture is introduced into a 4 liter round-bottomed flask fitted with a stirrer, a thermometer, an ascending cooland and an air supply:

1368.5 g of Cekanoic C10 acid

5 g of ditertiobutyl paracresol (polymerization inhibitor)

12.5 g of Hyamine 10X from ROHM & HAAS (reaction catalyst).

Air is bubbled through at the rate of 10 l/h and the mixture is heated to 100°C. At 100°C, one begins to add 1131.5 g of glycidyl methacrylate over 3 hours while keeping the temperature between 100 and 103°C. At the end of this addition, the temperature is maintained between 100 and 103°C until

a stable acid number is obtained, after which the product is cooled.

The above Examples 1 and 2 make it possible to obtain solutions of copolymers having a dry extract of about 57%. Their viscosity was of the order of 20 poises at 25°C.

The copolymers of the invention can be used in the preparation of varnishes and lacquers which can be cross-linked by reaction with polyisocyanates.

It is possible to adjust the properties of the products obtained by acting on the relative proportions of the styrene and methyl methacrylate. In particular, if it is desired to obtain a product having good external durability, it is necessary to use methyl methacrylate in preference to styrene, the latter having poor resistance to ultraviolet radiation.

PATENT CLAIMS

(We claim)

1. Copolymers which can be used in the preparation of varnishes and lacquers, characterized in that they contain the following constituents:

(a) 0 to 50% by weight of styrene,

(b) 0 to 72% by weight of methyl methacrylate, with the proviso that the sum of these two components reaches at least 23%,

(c) 10 to 30% by weight of hydroxyalkyl acrylate and/or methacrylate,

(d) 0 to 20% by weight of methacrylic acid,

(e) 8 to 20% by weight of glycidyl methacrylate and/or glycidyl acrylate, esterified by:

(f) 10 to 25% by weight of fatty acids which are saturated in C8 to C12,

the parts (a) to (f) together adding to 100%.

2. Copolymers in accordance with Claim 1, characterized in that the compounds (c) are chosen from the following group: 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate.

3. Copolymers in accordance with Claim 1, characterized in that the compounds (f) are linear or branched and of natural or synthetic origin.

4. Copolymers in accordance with Claim 1, characterized in that at least part of the methacrylic acid is replaced by acrylic acid.

5. A process for preparing the polymers in accordance with Claim 1 and which can be used for the production of varnishes and lacquers, characterized in that, in an appropriate solvent, one causes the copolymerization of monomers heated at a temperature chosen within the range 70° to 170°C, in which there is slowly added, while stirring in the presence of an agent which favors the polymerization, a mixture which consists of monomers chosen from the following and in the indicated range of percentages:

(a) 0 to 50% by weight of styrene,

(b) 0 to 72% by weight of methyl methacrylate, with the proviso that the sum of these two components reaches at least 25%

(c) 10 to 30% by weight of hydroxyalkyl acrylate and/or methacrylate,

(d) 0 to 20% by weight of methacrylic acid,

(e) 8 to 20% by weight of glycidyl methacrylate and/or glycidyl acrylate, esterified by:

(f) 10 to 25% by weight of fatty acids which are saturated in C8 to C12,

the parts (a) to (f) together totaling 100% by weight.

6. A process in accordance with Claim 5, characterized in that, as the polymerization solvent use is made of an appropriate solvent which is inactive with respect to the isocyanates, and which is chosen from alkyl benzenes, esters such as butyl acetate, the ether esters of diols such as methyl glycol acetate, ethyl glycol acetate.

7. A process in accordance with Claim 5, characterized in that the process is carried out in the presence of a conventional polymerization initiator of the type with free radicals.

8. A process in accordance with Claim 4, characterized in that the process is carried out in the presence of conventional chain transfer agents.

9. A process in accordance with Claim 5, characterized in that to the chosen polymerization solvent there is added the mixture of monomers at a temperature of 70 to 170°C, the addition being made over a period of several hours.

Translated by A. & R. Taylor